Fate of Mercury in Synthetic Gypsum Used for Wallboard Production

Topical Report, Task 1 Wallboard Plant Test Results

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April 2005

Cooperative Agreement No: DE-FC26-04NT42080

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ABSTRACT

This report presents and discusses results from Task 1 of the study "Fate of Mercury in Synthetic Gypsum used for Wallboard Production" performed at a full-scale commercial wallboard plant. Synthetic gypsum produced by wet flue gas desulfurization (FGD) systems on coal-fired power plants is commonly used in the manufacture of wallboard. This practice has long benefited the environment by recycling the FGD gypsum byproduct, which is becoming available in increasing quantities, decreasing the need to landfill this material, and increasing the sustainable design of the wallboard product. However, new concerns have arisen as recent mercury control strategies involve the capture of mercury in FGD systems. The objective of this study is to determine whether any mercury is released into the atmosphere when the synthetic gypsum material is used as a feedstock for wallboard production. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory (Cooperative Agreement DE-FC26-04NT42080), USG Corporation, and EPRI. USG Corporation is the prime contractor and URS Group is a subcontractor.

The project scope includes five discrete tasks, each conducted at various USG wallboard plants using synthetic gypsum from different FGD systems. The five tasks will include 1) a baseline test, then variations representing differing power plant 2) emissions control configurations, 3) treatment of fine gypsum particles, 4) coal types, and 5) FGD reagent types. For Task 1, three key process stacks in the wallboard plant were sampled using the Ontario Hydro Method. The stack locations sampled for each task will include a dryer for the wet gypsum as it enters the plant, a gypsum calciner, and, for Task 1 only, a dryer for the wet wallboard product. Also at each site, in-stream process samples will be collected and analyzed for mercury concentration before and after each significant step in wallboard production. The Ontario Hydro results, process sample mercury concentration data, and process data will be used to construct mercury mass balances across the wallboard plants.

Task 1 was conducted at a wallboard plant processing synthetic gypsum from a power plant that fires a high-sulfur bituminous coal. The power plant has a limestone forced oxidation FGD system, with the forced oxidation conducted in the reaction tank integral with the FGD absorber and no gypsum fines blow down. During the production of the synthetic gypsum used during this test, a selective catalytic reduction (SCR) system was in service for NO_X emissions control.

The results of the Task 1 stack testing, as measured by the Ontario Hydro method, detected only 1 to 2% of the gypsum or wallboard mercury content being evolved from any one stack. The total mercury loss across the wallboard plant represented about 5% of the incoming synthetic gypsum mercury content. Over 90% of the mercury detected by the stack testing was in the form of elemental mercury. The analyses of process samples indicated only 2% mercury loss from the gypsum across the wallboard plant. The differences between the percentage mercury loss determined by these two methods are discussed in the report.

Some additives and the paper used on the outer surfaces of the wallboard were found to contain small concentrations of mercury. Together they only accounted for 1% of the mercury content in the wet wallboard produced. It is not clear whether or not they significantly contributed to the small percentage mercury loss from the wet wallboard measured in the board dryer stack.

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INTRODUCTION

This report presents and discusses results from Task 1 of the study “Fate of Mercury in Synthetic Gypsum used for Wallboard Production” performed at a full-scale commercial wallboard plant. The objective of this project is to measure whether any mercury evolves from synthetic gypsum produced by wet flue gas desulfurization (FGD) systems on coal-fired power plants, when that material is used as a feedstock for wallboard production. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory (Cooperative Agreement DE-FC26-04NT42080), USG Corporation, and EPRI. USG Corporation is the prime contractor, and URS Group is a subcontractor.

Background

To address concerns about air quality, the U.S. Congress passed the Clean Air Act Amendments of 1990, which placed significant restrictions on sulfur oxide emissions. In order to reduce sulfur emissions and meet the Clean Air Act standards many electric utilities installed flue-gas-desulfurization (FGD) units. The FGD units combine the sulfur gases released during coal combustion with a sorbent, such as limestone or lime, which produces synthetic gypsum. The synthetic gypsum produced is commonly used as a feedstock for wallboard production. The reuse of the synthetic gypsum is environmentally beneficial and is also economically attractive for the power and wallboard industries. As sulfur oxide emissions become more regulated, greater amounts of synthetic gypsum will be created causing a large increase in volume of this material. The recycling of the material in wallboard manufacture limits the burden of adding the material to landfills. In addition, establishing wallboard manufacturing plants both near the power plants and population centers, increases the sustainable design of the wallboard product by reducing transportation and use of fossil fuels.

A number of mercury control strategy plans for U.S. coal-fired power generating plants involve the capture of oxidized mercury from flue gases treated by wet FGD systems. U.S. EPA estimates consider “co-removal” of mercury at high percentage an expected result for coal-fired plants that are equipped with selective catalytic reduction (SCR) for NO_X control and wet FGD systems for SO_2 control. SCR systems on bituminous coal fired plants have been observed to oxidize most of the elemental mercury in the SCR inlet gas. Also, a number of proposed mercury control processes involve using low-temperature catalysts or injected chemicals to oxidize elemental mercury and promote increased mercury removal across FGD systems.

For these processes to be effective at overall mercury control, the mercury must stay in the FGD byproducts and not be re-emitted to the atmosphere or into groundwater. Measurements by URS Group and others have indicated that nearly all of the mercury scrubbed from flue gases in most wet FGD systems ends up in the solid byproducts. Very little mercury is typically found in the FGD liquors. Thus, mercury stability in FGD solid byproducts is an important aspect of mercury capture in FGD systems.

Most FGD systems use lime or limestone reagent and employ forced oxidation to produce gypsum ($CaSO_4{\bullet}2H_2O$) as the solid byproduct. Much of the gypsum byproduct is reused, primarily as a feedstock for wallboard manufacturing. Those that do not produce gypsum instead produce a calcium sulfite hemihydrate ($CaSO_3{\bullet}½H_2O$) byproduct. Most calcium sulfite byproducts are landfilled, although some is reused as mine fill.

Approximately 70% of all of the FGD byproduct reuse in the U.S. is gypsum used as wallboard feedstock. During the year 2005, synthetic gypsum from FGD systems is expected to represent 30% of the U.S. wallboard plant feedstock.

This raises new technical questions: What is the fate of mercury in synthetic gypsum in the wallboard plant process? How much mercury is released into the atmosphere during the production of wallboard using synthetic gypsum? Is the amount of mercury released counterproductive to controlling mercury emissions from coal-fired power plants?

Even if mercury is not released in significant quantities during wallboard production, there remains a question as to the stability of mercury in the wallboard product. As an example, at the end of its product life cycle, most wallboard ends up in municipal landfills. What is the stability of mercury in wallboard produced from synthetic gypsum? Will the mercury leach into the acidic aqueous environment in a municipal landfill? This project is intended to collect data from commercial wallboard plants processing FGD synthetic gypsum to help answer these questions.

The Wallboard Production Process

Figure 1 shows an overview of the wallboard production process. In the process, synthetic gypsum is dried to produce "land plaster," which is gypsum that contains no free moisture, only chemically bound waters of hydration. The land plaster is then calcined to produce the "beta" form of calcium sulfate hemihydrate according to the following chemical reaction:

$$2\ CaSO_4{\bullet}2H_2O + \text{heat} \rightarrow 2\ CaSO_4{\bullet}½H_2O + 3\ H_2O$$

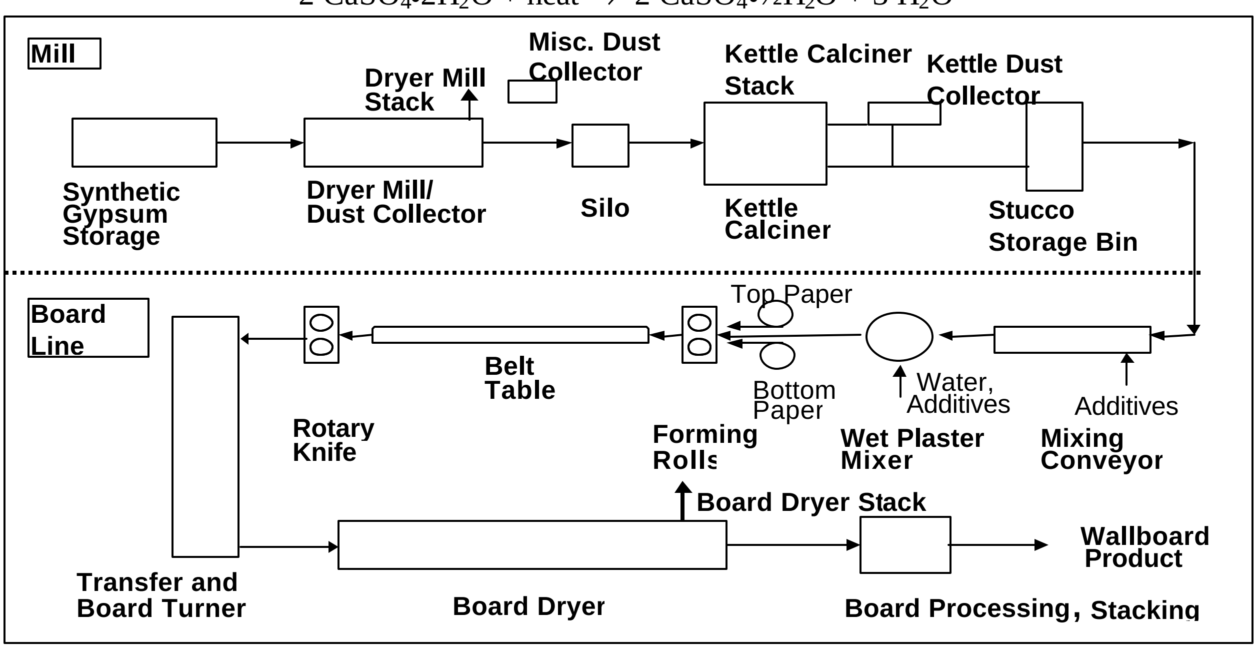

Figure 1. Simplified Schematic of the Wallboard Production Process.

The beta hemihydrate is also commonly called “stucco” or “plaster of Paris.” The stucco is subsequently mixed with water and a number of additives to form a slurry that is extruded between two sheets of paper to form the wallboard. The hemihydrate re-hydrates to form gypsum by the reverse of the reaction shown above. This re-hydration consumes much of the water in the slurry, and causes the gypsum formed to set up as a cohesive solid. The wet board travels down a conveyor belt while it is setting up. After adequate residence time to set up, the board is cut to approximate length then dried to remove free moisture (excess water not consumed by the re-hydration reaction). The dried product is cut to final length then stacked for shipping.

The initial gypsum drying and calcining steps described above occur in a section of the plant called the mill. The dryers are typically direct gas fired. Their purpose is to remove the free moisture in the synthetic gypsum (typically 8 to 12% by weight of the raw material) prior to calcining. The dryers consequently operate at temperatures well below the gypsum calcining temperature of 262^{o}F. The solids are dried by direct contact between the wet particles and the hot flue gas. The moisture-free synthetic gypsum (land plaster) is collected in mechanical collectors or a fabric filter and placed in intermediate storage silos prior to feeding to the calciners.

In the calcining step, the solids temperature must be raised above 262^{o}F to promote release of 1-½ waters of hydration, but must be kept below 325^{o}F to avoid forming anhydrous calcium sulfate (no remaining waters of hydration). The calciners used at the wallboard plant tested are indirect-fired kettle calciners, so the vent gas from the solids side of the kettle is primarily a mixture of steam and air. A kettle calciner dust collector removes fine stucco particles from this vent gas. The recovered fine particles are then incorporated into the product stucco. The stucco leaving the kettle is cooled and placed in a bin for intermediate storage, to provide a buffer between the mill and board line.

In the board line, the cooled stucco from the silo is fed to a mixer, where “gauging” water is added to form a viscous slurry. The gauging water is typically of high quality (e.g., potable water). A number of proprietary additives are mixed with the wet slurry produced from the stucco.

This wet slurry is continuously extruded between two sheets of paper that are fed from rolls above and below the extruder. One type of paper is used for the face of the wallboard product and another for the back. The dimensions of the formed board are set by rollers and edge shoes. The formed board travels down a long conveyor belt that provides residence time for the stucco to re-hydrate and take a set. At the end of this belt, the formed board is cut and inverted so the face paper is facing up.

The board then enters a dryer. The dryer is zoned to operate over a range of temperatures, typically over 400^{o}F at the dryer entrance and about 200^{o}F at the exit. However, the board residence time in the dryer is controlled to limit the temperature of the dried board. This temperature must be limited to avoid any of the set-up solids re-calcining to the hemihydrate form. Thus, the bulk of the re-hydrated gypsum solids in the wallboard product stay well below 262^{o}F in temperature. From the dryer, the dried board is cut to final size, has end tape applied, and is stacked for shipment.

Any potential mercury losses during the wallboard process are assumed to occur during the thermal processes, with losses most likely during the calcining step. The synthetic gypsum particles are raised to the highest temperature in the process during this step (above 262°F). Losses are also possible from the synthetic gypsum dryer and the finished wallboard dryer, although the maximum temperatures to which the gypsum is raised are lower in the dryers (approximately 170°F to 230°F).

Project Overview

This project is intended to provide information about the fate of mercury in synthetic gypsum produced by FGD systems on coal-fired power plants, when used as feedstock for wallboard production. Solid samples from various locations in the wallboard process, including the wallboard product, are being collected and analyzed for mercury content. Simultaneous flue gas measurements are being made using the Ontario Hydro Method to quantify any mercury releases to the atmosphere during wallboard production. Most of the testing is concentrated in the mill processes where the synthetic gypsum is dried and calcined. Any potential mercury releases from the synthetic gypsum solids are thought to result from thermal desorption. It is in the mill portion of the process where the feedstock sees the highest process temperatures and where the evolution of waters of hydration may promote mercury desorption.

A limited amount of testing is being conducted in the downstream board line, where the calcined gypsum is slurried, mixed with proprietary additives and formed into wallboard. The project plan was for the board dryer kiln stack flue gas to only be measured for mercury content at the first test site, as described below. Lesser mercury release is expected in the board kiln because it is downstream of the mill, and the re-hydrated gypsum solids typically see lower temperatures than in the mill.

The solid and flue gas mercury concentration and plant process data are being used to calculate mercury balances across the operating wallboard plant.

Samples of each synthetic gypsum tested are being evaluated in laboratory simulated calcining tests to provide comparison data and evaluate a lab technique for screening synthetic gypsum samples. Also, wallboard produced from synthetic gypsum will be leached according to the Toxicity Characteristic Leaching Procedure (TCLP) to provide an indication whether wallboard disposed of in municipal landfills will have a tendency to release mercury into groundwater.

The project will investigate wallboard produced from a variety of synthetic gypsum sources, all from FGD systems on coal-fired power plants, but from different coal types, power plant emissions control configuration and FGD conditions. The project is structured in five tasks. As shown in Table 1, each task involves one commercial wallboard plant test. This report summarizes the results from Task 1, which investigated a commonly used synthetic gypsum feedstock, produced by a power plant that fires high-sulfur bituminous coal and that has a limestone, forced oxidation (LSFO) FGD system that produces wallboard grade gypsum byproduct and that has an SCR for NO_X control. Additional tasks will include tests on synthetic gypsum feedstocks produced from:

- The same plant included in Task 1, but without the SCR operating (SCR catalyst bypassed). Since SCR catalysts have been observed to promote mercury oxidation, taking the SCR out of service may impact the amount of mercury captured in the FGD byproduct and could impact mercury losses during wallboard production,

- A high-sulfur, bituminous LSFO plant that employs gypsum fines blow down,

- A plant that fires a low rank coal (Texas lignite) rather than bituminous coal, and

- A plant that uses lime rather than limestone FGD reagent, and employs external rather than in situ forced oxidation.

Each of these variables is thought to impact the amount of mercury in the synthetic gypsum feedstock and/or possibly impact the stability of that mercury in the wallboard production process.

Table 1. Project Test Matrix

Task	**1**	**2**	**3**	**4**	**5**
Synthetic Gypsum Source:					
Power Plant	A	A	B	C	D
Coal Type	High sulfur bituminous	High sulfur bituminous	High sulfur bituminous	Texas lignite	High sulfur bituminous
FGD Reagent	Limestone	Limestone	Limestone	Limestone	Lime
Forced Oxidation Mode	In Situ	In Situ	In Situ	In Situ	External
Gypsum Fines Blow Down?	No	No	Yes	No	Yes
SCR Status	On Line	Bypassed	On Line	No SCR	TBD*
USG Wallboard Plant Tested	1	1	2	3	1

*To be determined based on the time of year of the test

To investigate all five of these synthetic gypsum feedstocks, tests will be conducted at three different USG wallboard plants, since no one plant uses all five as a feedstock. The relationship between synthetic gypsum types and USG plants proposed for investigation is summarized in Table 1. Note that the power plants and USG wallboard plants are not identified by name, only by letter or number codes, in accordance with an agreement for anonymity at the beginning of the project.

This report presents and discusses the results of the wallboard plant testing conducted as part of Task 1, including Ontario Hydro measurements in the dryer mill, kettle calciner, and board dryer kiln stacks, process sample mercury content, process data, and mercury balance results. Planned laboratory evaluations, including simulated gypsum calcining tests and mercury leaching from wallboard product samples by TCLP, have not been conducted yet and will be reported later in the project.

Report Organization

The remainder of this report is organized into four sections: Experimental, Results and Discussion, Conclusion, and References. The section entitled Experimental describes the experimental methods used to conduct the mercury testing at a commercial wallboard plant as part of Task 1, including stack testing, process sampling, and off-site chemical analyses. The Results and Discussion section presents results from the stack testing, process sample analyses, process data collected, and mercury balance calculations. The Conclusion section provides preliminary conclusions that can be made from the results of this first of five commercial wallboard plant mercury tests.

EXPERIMENTAL

A description of the project test matrix was provided in the Introduction section. This section begins with an explanation of the rationale used for choosing this particular FGD synthetic gypsum for the base case test conditions. The remainder of the section presents details of how the first wallboard plant mercury test was conducted, including stack testing by the Ontario Hydro method, process sample collection and analyses, and process data collection.

Rationale for Selecting the Synthetic Gypsum Tested

The first wallboard plant test involved testing the fate of mercury in synthetic gypsum from a high-sulfur, bituminous-coal-fired power plant equipped an operating SCR and with an LSFO FGD system that does not employ fines blow down (Power Plant A). This combination was selected for the first test because the synthetic gypsum produced at Power Plant A has a relatively high mercury content. As explained below, higher mercury content should enhance the accuracy of the tests. Furthermore, previous laboratory testing funded by EPRI[1] and initial full-scale tests by USG[2] suggest that small measurable mercury losses could be expected from this feedstock during wallboard production. For these reasons, it was thought that testing this material as the first case could be a USG worst-case scenario for potential mercury losses during wallboard production.

Previous testing has shown that, at least for some plants that fire high-sulfur bituminous coal, having an SCR in service tends to increase the percentage oxidation of mercury in the flue gas upstream of an FGD system, and to increase the percentage capture of mercury in the FGD.[3,4] Many plants that are equipped with SCR only operate them during the “ozone season,” from May 1 through September 30 each year, and bypass the SCR catalyst the remainder of the year. For such plants, one might expect that synthetic gypsum produced from their FGD systems would contain more mercury with the SCR operating during the ozone season than that produced during the remainder of the year.

Gypsum fines blow down is believed to be an important variable. Most synthetic gypsum used as a wallboard plant feedstock is subject to a number of quality control specifications by the wallboard manufacturer, including maximum moisture content, minimum gypsum content, maximum chloride content, and particle size distribution. A number of FGD variables affect the ability to meet the solids particle size distribution specification. These variables include the gypsum crystal residence time in the FGD absorber loop, FGD reagent chemical composition, and the amount of physical abrasion to which the crystals are exposed as they are recirculated and dewatered. Some FGD systems cannot meet the wallboard manufacturer’s particle size specification unless they separate a portion of the byproduct containing the smallest particle sizes. This separation is typically accomplished with hydrocyclones. The separated fines are either discarded or sold for other uses. Other plants need to purge a portion of the hydrocyclone overflow as a means of limiting chloride buildup in the FGD liquor. These plants blow down gypsum fines as part of the chloride purge. In still other plants, there is no need to separate the fines and/or purge chlorides, and the fines are included in the byproduct sent to the wallboard plant.

Laboratory testing conducted by URS for EPRI has indicated that the mercury concentration in gypsum fines can be as much as an order of magnitude higher than in the larger particles.[1] This suggests that mercury precipitates and/or adsorbs at gypsum surfaces, since the fines have a much higher surface area to mass ratio than larger particles. It is also possible that mercury adsorbs on or precipitates with fine particles of impurities that enter the FGD system with fly ash in the flue gas or with the FGD reagent. Upwards of half of the mercury removed by the FGD system can be in the fines. Fines blow down therefore significantly lowers the mercury concentration in the synthetic gypsum byproduct going to the wallboard plant.

Since the plant providing the feedstock for this first test does not employ fines blow down, it was expected to have a higher mercury content in the synthetic gypsum byproduct than would a similar plant with fines blow down. This byproduct might thermally evolve more mercury in the wallboard mill than would a byproduct with the fines removed and a lower total mercury concentration.

The first case was chosen to represent conditions that, for the reasons described above, were believed most likely to show measurable mercury losses during the wallboard production process. It was anticipated that the other four synthetic gypsum feedstocks, as described in the Introduction, would show reduced mercury evolution, but full-scale testing would be required to confirm or deny such assumptions.

Commercial Wallboard Plant Test Procedures

Commercial wallboard plants often operate with a blend of feedstocks from a number of FGD systems. Rarely does one power plant generate enough synthetic gypsum to feed the entire production of a modern wallboard plant, so most plants process synthetic gypsum from two or more power plants. Each synthetic gypsum has unique processing conditions within the wallboard plant process. Therefore, to minimize excessive swings in wallboard plant operating conditions, most plants blend the available feedstocks to produce an “average” material for processing.

However, for this test, Wallboard Plant 1 was operated on 100% feedstock from Power Plant A. It would be difficult to elucidate the effects of power plant and FGD variables on mercury losses during wallboard production if synthetic gypsum blends were being processed during measurements. Also, the feedstock to the mill typically contains recycled material, which can include recycled wallboard, wallboard samples, material recycled from the calciner during shut downs, etc. Because recycle consists of material from a variety of sources, it was felt that recycle would add variability to the incoming feed mercury concentration and possibly its stability. Therefore, the wallboard plant test was conducted with no recycle feed to the plant and during the use of Power Plant A synthetic gypsum only.

Two days of sampling were conducted in USG Wallboard Plant 1, with the first day in the mill and the second day in the board line as described below. Figure 2 illustrates the wallboard production process. Process streams that were sampled as part of the test, as described below, are marked with “S” followed by a number that represents a sample location. The sample numbers are used in the data tables later in the report.

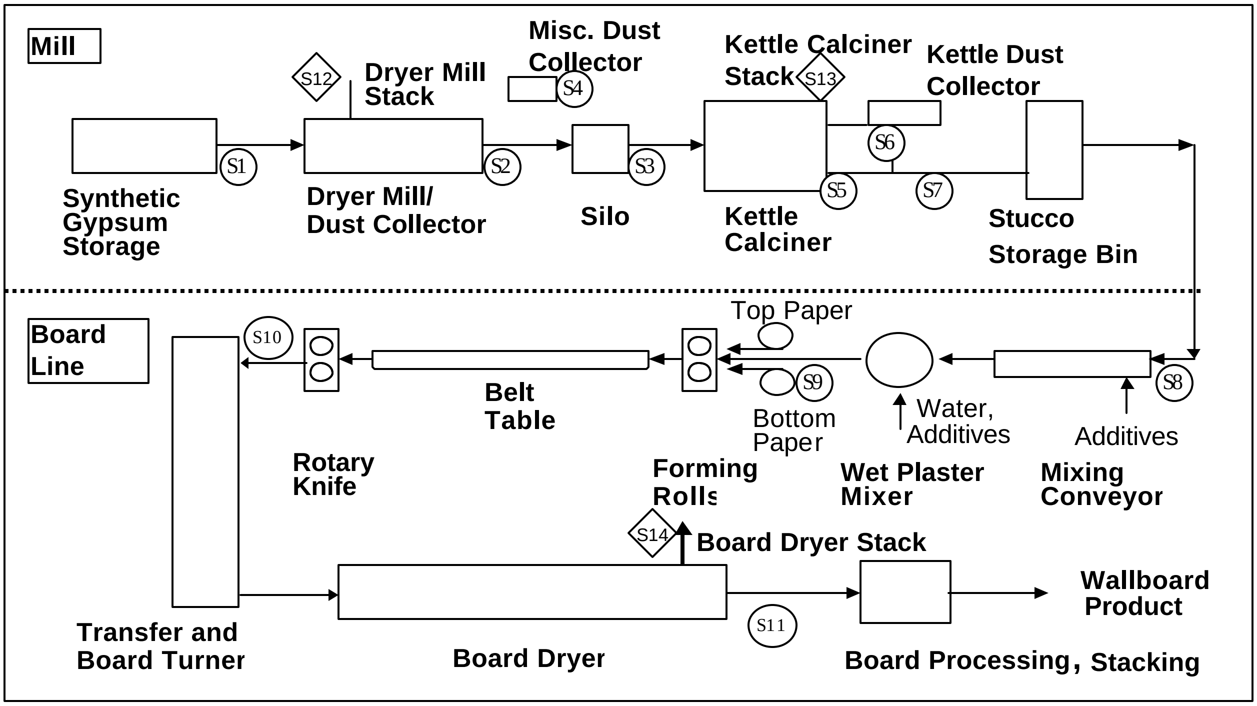

Figure 2. Schematic of a Wallboard Plant Showing Task 1 Sampling Locations

Day 1 – Mill Testing

Stack Sampling

On the first test day, simultaneous gas measurements were conducted using the Ontario Hydro Method (ASTM D6784-02) on a gypsum dryer (dryer mill) stack and the downstream kettle calciner steam stack on a single train of the plant. However, note that the method was modified slightly for sampling at the kettle calciner steam stack, as described below. Triplicate runs were made at each of these two locations.

The kettle calciners are indirect-fired vessels. The gaseous stream from the calciner that could contain mercury from the synthetic gypsum is the "steam stack," which is a mixture of the water calcined from the gypsum when forming stucco ($CaSO_4 \bullet ½H_2O$) and aeration air introduced at the bottom of the kettle. The other stack from the kettle calciner contains the flue gas from the burners, which are natural gas fired. This stream is not expected to have measurable mercury content.

The steam stack gas is significantly wetter than and typically does not contain species present in coal flue gases (e.g., CO_2, SO_2 and HCl), for which the Ontario Hydro Method was developed and validated. Consequently, the method was modified slightly to ensure proper sampling and speciation under these conditions.

As mentioned above, the kettle calciner steam stack gas is mostly water. Since the Ontario Hydro Method measures mercury in a dry gas sample, it was speculated that the mercury content of the dry gas, which represents less than half of the total gas stream, could be greater than 100 μg/Nm^3, which is the stated upper measurement limit for which the method was developed.[5] When sampling above this limit, there was concern that reagents in the collection impingers would be depleted. To avoid this issue and to reduce the quantity of water collected in the impingers during the run, the Ontario Hydro runs on the kettle calciner were reduced in duration from 120 minutes to approximately 60 minutes.

The dryer mill is direct fired, so its stack gas is a true flue gas and the standard Ontario Hydro Method should be appropriate for sampling this stream. Therefore, the dryer mill Ontario Hydro sampling runs were for a full 120 minutes, as per the method. The kettle calciner sampling runs were started about 30 minutes after the dryer mill runs began, so the kettle calciner sample would be collected in the middle of the dry mill sample collection period.

Process Sampling

During each of the three runs, process samples were collected from the dryer feed solids, dryer product solids (land plaster to intermediate silo), calciner feed (land plaster from intermediate silo), and calciner product stucco to the stucco storage bin. These four streams represent the feeds and products for the dryer mill and kettle calciner. Three additional solid stream samples were collected: the solids collected in a "miscellaneous" dust collector from transfer points in the mill, which are added to the calciner feed solids; the solids collected from the kettle calciner dust collector, which are incorporated into the product stucco; and the stucco solids exiting the kettle calciner, prior to having the dust collector solids added. These three sample types were analyzed for mercury concentration, but these data were not used for any of the mercury balance or mercury loss calculations.

All seven of these process solids samples were collected as "grab" samples during the middle part of each Ontario Hydro run. No attempt was made to collect time-integrated samples, e.g., by collecting small sample aliquots at periodic intervals throughout the Ontario Hydro sampling periods and compositing the aliquots into a single sample. It was felt that the incoming raw gypsum would be homogenous enough that one grab sample per run would adequately represent the feedstock and other process solids. These 21 grab samples (seven locations times three Ontario Hydro runs) were subsequently analyzed for mercury content in URS' Austin, Texas laboratory.

Process data were collected during each of the three run periods, including dryer and calciner feeder speeds and operating temperatures. These data were recorded as two-hour trend plots for each parameter.

Day 2 – Board-Line Testing

Stack Testing

On the second test day, triplicate Ontario Hydro Method measurements were made on the board dryer kiln stack gas. The timing of the second day measurements was coordinated with the plant to approximately correspond with the processing of stucco material calcined the previous day. This took into account the residence time in the stucco storage bin between the mill and board line.

Process Sampling

During each of the triplicate Ontario Hydro runs, samples were collected of the feed stucco, the slurry fed to the board forming machine, and the wet and dry product wallboard. Water and a number of proprietary additives are added to the stucco when mixing the slurry prior to the board forming step. The water, each of these additives, and the paper used during board forming were also sampled once during the day, to evaluate their impact on the mercury content of the slurry and the wallboard. Triplicate samples of the additives and paper were not deemed to be necessary, as each is fed from a large silo, storage tank, or roll that should have been relatively homogenous over the course of the three Ontario Hydro runs. Note that, because the composition and dosages of the additives are considered proprietary, the results from sampling additives and the paper are reported only as their percent contribution to the total mercury content in the wet board. No individual additive feed rate or mercury concentration data are reported, nor are the chemical compositions or names of these additives.

As for the Day 1 testing effort, key process data were collected throughout the test day. These data were collected as screen prints from the process control software during the middle of each of the three Ontario Hydro runs. Trend plotting of these data for the run duration was not available. Board production parameters do not change rapidly, so one screen print per sampling period should be representative of conditions for that run. For the board line, these data include the stucco feed rate, water and additive feed rates (not included in this report), paper thickness and weight, board production rate, and the dryer flue gas temperatures.

As the two-day sampling effort was completed, all process and Ontario Hydro Method samples were recovered, stabilized, and labeled, then shipped to URS' Austin, Texas laboratories for mercury analyses. Method blanks and reagent blanks for the Ontario Hydro Method samples were included with the sample sets as a quality assurance/quality control measure.

Representative coal samples and power plant and FGD process data were also collected by the utility producing the synthetic gypsum being evaluated. The coal samples will be analyzed for ultimate and proximate analyses, chlorine and mercury content. The coal data along with the power plant and FGD process data will be used to document typical conditions under which the synthetic gypsum evaluated was produced.

All of the mill and board-line process samples collected were analyzed for mercury content, by cold vapor atomic absorption after digestion in hydrofluoric acid. A number of samples were analyzed for other parameters, including gypsum moisture content, particle size distribution, specific surface area, and chloride content.

The mercury concentration analytical results, along with plant process data, were used to construct a mercury balance across the mill and the board line. The mercury balances show individual stream flow rates and mercury concentrations (except for the additives used in the board line), the amount of mercury entering and leaving the plant in each process stream, and overall mercury mass balance closures. Data are shown for individual sampling runs and as means and 95% confidence intervals about the means for the triplicate measurements.

The coal data, power plant data, and FGD process data from the power plant producing the synthetic gypsum evaluated have not yet been collected and tabulated. These data will be reported later in the project.

RESULTS AND DISCUSSION

This section provides technical results for the Task 1 wallboard plant test. Results presented include gypsum and process sample analysis results, Ontario Hydro flue gas measurement results, plant process data, and mercury balance results. Each type of result is discussed in a separate subsection below.

Gypsum and Process Sample Mercury Analysis Results

Table 2 summarizes the results of mercury and moisture content analyses conducted by URS on the raw gypsum, stucco product, and intermediate process samples collected during the mill test (July 27, 2004). Table 3 shows results for additional characterization of these samples conducted by USG, including mercury and moisture content. Table 4 shows the results for mercury and moisture analyses conducted by URS on stucco, wallboard product, and intermediate process samples collected during the board-line test (July 28, 2004).

Table 2. Task 1 Raw Gypsum and Mill Process Sample Mercury and Moisture Analyses, URS Results

Sample Number	Sample Description	Mercury Content, mg/g (dry basis)					Moisture Content, wt% as received			
		Run 1	Run 2	Run 3	Mean	95% C.I.*	Run 1	Run 2	Run 3	Mean
S1	Raw Gypsum Feed to Dryer Mill	0.98	0.94	0.98	0.96	±0.03	10.5	12.5	12.6	11.9
S2	Land Plaster from Dryer Mill	0.93	0.93	1.00	0.95	±0.05	<1	<1	<1	-
S3	Land Plaster to Kettle Calciner	0.96	0.96	0.98	0.96	±0.01	<1	<1	<1	-
S4	Misc. Dust Collector Solids to Kettle Calciner	1.52	1.50	1.60	1.54	±0.06	<1	<1	<1	-
S5	Kettle Calciner Product, as measured	1.07	1.09	1.10	1.09	±0.02	<1	<1	<1	-
	Kettle Calciner Product, dry gypsum basis	0.90	0.92	0.93	0.92	±0.01	<1	<1	<1	-
S6	Kettle Calciner Dust Collector Solids, as measured	2.46	2.57	2.42	2.48	±0.09	<1	<1	<1	-
	Kettle Calciner Dust Collector Solids, dry gypsum basis	2.07	2.17	2.04	2.09	±0.07	<1	<1	<1	-
S7	Product Stucco, as measured	1.09	1.15	1.14	1.13	±0.04	<1	<1	<1	-
	Product Stucco, dry gypsum basis	0.92	0.97	0.96	0.95	±0.03	<1	<1	<1	-

*95% Confidence Interval of mean

Table 3. Task 1 Raw Gypsum and Mill Process Sample Characterization, USG Results

Sample	Run	Moisture Content, wt%		Mercury Content, μg/g		Soluble Salts, ppm		Particle Size Distribution (microns)				Blaine Surface Area, cm^2/gm
		Free	Total	As measured, dry basis	Dry Gypsum basis	Total	Cl^-	Mean Dia.	Particle Size at % Less Than: 10%	50%	95%	
S1 – Raw Gypsum Feed to Dryer Mill	1	9.55	20.1	1.00	1.00	148	36.0	53.1	24.7	48.9	101	1,065
	2	10.8	20.0	1.07	1.07	149	34.0	53.5	24.1	48.6	104	1,071
	3	11.3	20.0	1.05	1.05	139	30.5	53.2	23.9	48.5	104	1,034
Mean		10.5	20.0	1.04	1.04	145	33.5	53.2	24.2	48.6	103	1,057
95% C.I.*		±1.0	±0.0	±0.04	±0.04	±6	±3.2	±0.3	±0.5	±0.2	±2	±22
S2 – Land Plaster from Dryer Mill	1	0.13	19.2	0.98	0.98	96.9	37.2	52.1	23.1	47.9	101	1,142
	2	0.14	19.2	0.94	0.94	72.2	41.4	53.5	24.8	49.4	102	1,111
	3	0.10	19.1	1.03	1.03	89.3	36.9	50.8	21.8	46.6	99.5	1,152
Mean		0.1	19.2	0.98	0.98	86.1	38.5	52.1	23.2	48.0	101	1,135
95% C.I.		±0.0	±0.1	±0.05	±0.05	±14.3	±2.8	±1.5	±1.7	±1.6	±1	±24
S3 – Land Plaster to Kettle Calciner	1	0.12	18.8	1.02	1.02	103	30.6	51.9	23.1	47.6	101	1,128
	2	0.12	18.9	1.05	1.05	123	31.9	53.2	24.6	49.2	101	1,160
	3	0.14	18.6	1.10	1.10	117	29.5	52.6	22.9	48.1	104	1,149
Mean		0.13	18.8	1.06	1.06	114	30.7	52.5	23.5	48.3	102	1,146
95% C.I.		±0.0	±0.2	±0.05	±0.05	±12	±1.4	±0.7	±1.1	±0.9	±2	±18
S4 – Misc. Dust Collector Solids to Kettle Calciner	1	0.74	6.86	1.75	1.47	225	35.0	40.4	12.6	36.3	86.5	2,777
	2	0.77	6.82	1.68	1.42	209	55.1	41.9	14.0	38.0	88.8	2,638
	3	0.83	6.79	1.79	1.51	175	67.3	42.3	13.2	36.6	91.4	2,811
Mean		0.78	6.82	1.74	1.47	203	52.5	41.5	13.3	37.0	88.9	2,742
95% C.I.		±0.05	±0.04	±0.06	±0.05	±29	±18.5	±1.1	±0.8	±1.1	±2.8	±104
S5 – Kettle Calciner Product	1	0.67	6.43	1.20	1.01	179	61.3	52.0	23.4	47.9	101	1,934
	2	0.74	6.41	1.20	1.01	156	57.0	50.6	22.4	46.7	97.6	2,021
	3	0.68	6.43	1.25	1.06	165	59.0	51.3	22.6	47.2	100	1,984
Mean		0.70	6.42	1.22	1.03	167	59.1	51.3	22.8	47.2	99.4	1,980
95% C.I.		±0.04	±0.01	±0.03	±0.03	±13	±2.4	±0.8	±0.6	±0.7	±1.8	±49
S6 – Kettle Calciner Dust Collector Solids	1	1.06	7.87	2.49	2.10	235	79.6	31.2	8.0	28.3	67.5	3,350
	2	0.70	8.10	3.04	2.57	234	75.0	29.9	7.0	27.2	65.0	3,542
	3	1.08	7.98	2.69	2.27	244	72.6	31.4	7.8	28.4	68.2	3,454
Mean		0.9	8.0	2.74	2.31	237.6	75.7	30.8	7.6	28.0	66.9	3,449
95% C.I.		±0.2	±0.1	±0.32	±0.27	±6.6	±4.0	±0.9	±0.6	±0.7	±1.7	±109
S7 – Product Stucco	1	0.84	6.47	1.20	1.01	185	55.8	52.3	22.7	47.4	103	1,954
	2	0.67	6.48	1.25	1.05	160	51.3	51.0	22.2	46.8	99.4	2,043
	3	0.57	6.51	1.22	1.03	189	51.3	51.1	22.3	47.1	99.3	1,977
Mean		0.69	6.49	1.22	1.03	178	52.8	51.5	22.4	47.1	101	1,991
95% C.I.		±0.15	±0.02	±0.03	±0.03	±17	±2.9	±0.8	±0.3	±0.4	±2	±52

*95% Confidence Interval of mean

Table 4. Task 1 Stucco, Wallboard Product and Intermediate Process Sample Mercury Analyses, URS Results

Sample Number	Sample Description	Mercury Content, μg/g (dry basis)					Moisture Content, wt% as received			
		Run 1	Run 2	Run 3	Mean	95% C.I.	Run 1	Run 2	Run 3	Mean
S8	Stucco Feed, as measured	1.12	1.14	1.10	1.12	±0.02	<1	<1	<1	<1
	Stucco Feed, dry gypsum basis	0.94	0.96	0.93	0.94	±0.02	<1	<1	<1	<1
S9	Slurry to Forming Rolls	1.00	0.98	0.95	0.98	±0.03	30.7[#]	30.9[#]	30.0[#]	30.5[#]
S10	Wet Wallboard	0.91	0.90*	0.91*	0.91	±0.01	24.1*	26.4*	24.5*	25.0
S11	Dry Wallboard Product	0.94	0.98*	0.94*	0.95	±0.02	<1	<1	<1	<1

*Average for two samples collected during Ontario Hydro run period
[#] Moisture content measured after sample set up, consuming some free moisture to rehydrate the stucco

In each of these three tables and throughout this section of the report, a mean and a 95% confidence interval about that mean are shown for key values in the table. The mean values represent the arithmetic average of the results from three runs, while the 95% confidence interval is a measure of observed variability of that value during the three runs. Specifically, the 95% confidence interval represents a range above and below the mean for the three runs over which we have a 95% confidence level that the true average for these three measurements would lie. The 95% confidence interval values were all calculated using the “CONFIDENCE” worksheet function in Microsoft Excel 2003® spreadsheet software.

The results from the URS analyses in Table 2 show that the raw gypsum feedstock, product stucco, and intermediate samples were relatively consistent in mercury content from run to run. The 95% confidence intervals about the mean values, also shown in the table, represent relatively small percentages of the measured values. The raw gypsum feed contained a mean value of 0.96 ppm, which was nominally the expected value for this gypsum, and 12% moisture, which is within the typical range for FGD gypsum. The results of USG analyses in Table 3 show slightly higher mean mercury concentrations (1.04 ppm average) and slightly lower moisture content (10.5%). However, the agreement between the two laboratories’ analyses can be considered quite acceptable. When considering the 95% confidence intervals about mean values in the two sets of analyses, the results nearly overlap.

It is interesting to note that in both the URS and USG sets of chemical analyses results, both dust collector solid streams showed significantly higher mercury concentrations than the other process streams. This is likely because it is the finer gypsum and gypsum impurity particles, and land plaster or stucco formed from these particles, that are collected in the dust collectors. Previous EPRI-funded results have shown that gypsum fines tend to have higher mercury content than the bulk gypsum.[1] The particle size distribution results in Table 3 show that the dust collector solids are, in both cases, finer than the bulk land plaster or stucco solids. In fact, the data in Table 3 show a linear, inverse correlation between mean particle size and measured mercury concentration ($r^2 = 0.96$).

Also, note that, notwithstanding potential mercury losses in the kettle calciner, mercury should be more concentrated in the kettle calciner product and in the product stucco than in the upstream samples, because of the evolution of 1½ waters of hydration in the calciner. For this reason, additional rows of data are shown in Table 2 expressing the mercury content in the stucco samples (S5, S6 and S7) on a dry gypsum basis. This accounts for the effects of the loss of waters of hydration by the stucco. Similarly, a column has been added to Table 3 showing all of the solids analysis results on a dry gypsum basis. The corrected values can be compared directly to see apparent mercury losses across the dryer mill and kettle calciner.

The results from the board-line testing in Table 4 show that the mean mercury concentration in the stucco feed to the wallboard plant was almost identical to the mean for the product stucco going to the stucco storage bin the day before. This suggests that the attempt to time-phase the board-line sampling to reflect the stucco produced in the mill the day before was successful, and/or that the stucco mercury concentration is relatively consistent for this feedstock.

Conversely to what was described for the kettle calciner, in the board line, the slurry and wallboard should have lower mercury concentrations than the feed stucco due to the 1½ waters of hydration gained on re-hydration of the stucco. To account for this effect, a row has been added to Table 4 showing the feed stucco mercury concentration on a dry gypsum basis. This allows any loss of mercury from the feed stucco to be observed directly by comparing mercury concentrations of the feed and product on a common dry gypsum basis. However, the effects of mercury in the additives, water, and paper added in the board line on the mercury content of the wallboard product must also be considered, as discussed later in this section in the mercury mass balance discussion.

Ontario Hydro Stack Sampling Results

The Ontario Hydro Method stack sampling results are summarized in the following tables. Table 5 summarizes gas flow rate, temperature, and major component concentrations. The results in Table 5 show that the dryer mill stack gas composition was consistent with a very dilute flue gas from natural gas firing, with only 2% CO_2 and 18% oxygen. The moisture content was relatively high at 16% due to the free moisture from the gypsum that is evolved in the dryer. The dryer mill flue gas temperature was less than 200°F, as would be expected because of the need to keep the dried gypsum below its initial calcining temperature of 262°F.

The kettle calciner results for exhaust gas composition were somewhat surprising. Because the kettle calciner is indirect fired, it was expected that the flue gas major components would consist of nothing but air and water. However, the gas composition was measured to contain more CO_2 and less oxygen than the dryer mill flue gas, which indicates that a significant fraction (30 to 40%) of the stack gas was flue gas from the combustion of natural gas. This is apparently an indication of a flue gas leak into the indirect-fired side of this kettle, perhaps due to a leaking tube or tubesheet.

Table 5. Task 1 Ontario Hydro Results – Summary of Exhaust Gas Conditions

Sample Number	Run No.	Date (2004)	Time (24-h)	Flow Rate		Temperature (°F)	H_2O (%)	CO_2 (%)	O_2 (%)
				acfm*	dscfm#				
Dryer Mill (1 of 2)									
S12	1	7/27	0846-1057	53,600	37,100	178	15.8	2.0	18.0
	2	7/27	1147-1352	54,500	37,700	179	15.9	2.0	18.0
	3	7/27	1455-1659	54,800	37,900	179	15.7	2.0	18.0
	Mean			54,300	37,600	178	15.8	2.0	18.0
Kettle Calciner (1 of 2)									
S13	1	7/27	0920-1020	13,900	4,420	262	56.2	5.0	15.0
	2	7/27	1219-1324	12,400	3,990	262	55.6	5.0	15.0
	3	7/27	1527-1632	13,000	4,170	261	56.1	4.0	15.0
	Mean			13,100	4,190	262	56.0	4.7	15.0
Board Dryer Kiln (1 of 1)									
S14	1	7/28	1146-1305	180,500	81,000	224	41.5	5.0	15.0
	2	7/28	1425-1622	159,200	71,600	226	41.3	4.0	15.0
	3	7/28	1716-1846	167,600	75,400	225	41.5	4.0	15.0
	Mean			169,100	76,000	225	41.4	4.3	15.0

*acfm = Actual cubic feet per minute at stack conditions
#dscfm = Dry standard cubic feet per minute; standard conditions are 68°F, 29.92 in.Hg, and 0 percent moisture

The measured moisture content of the kettle calciner steam stack gas was quite high, at 56%, mostly due to the waters of hydration released from the gypsum. Given the evidence seen of a flue gas leak into the indirect-fired side of the calciner, one could speculate that the dry flue gas rate might have been lower and the moisture content might have been higher without such a leak.

The board dryer kiln stack had by far the largest flue gas flow rate measured, although this stream represents treating the entire board-line production while the dryer mill and kettle calciner measurements were for only one of two parallel processing trains. The board dryer gas conditions showed more CO_2 and less oxygen than the dryer mill, indicating a more concentrated flue gas and less air dilution, consistent with the higher exit temperature in the board dryer stack.

Table 6 summarizes the mercury concentration and mass rate data. These results show that for all three stacks, the mercury was almost entirely in the elemental form (Hg^0). This is quite surprising, given that it is predominantly water-soluble oxidized mercury (Hg^{+2}) that is removed in wet FGD systems, while elemental mercury is virtually insoluble and not removed at significant percentages. There is no clear explanation for this phenomenon. Note that in the elemental form, mercury is not expected to readily deposit near the point of emission but ascends into the atmosphere and contributes to the overall global cycle.[6]

Table 6. Task 1 Ontario Hydro Results – Speciated Mercury Emissions Data

Sample Number	Run No.	Date (2004)	Time (24-h)	Concentration ($\mu g/Nm^3$)* Particle-Bound, Hg^P	Oxidized, Hg^{+2}	Elemental, Hg^0	Total Hg	Total Mercury Emission Rate (lb/h)#
Dryer Mill (1 of 2)								
S12	1	7/27	0846-1057	0.39	<0.10	12.2	12.6	1.63×10^{-3}
	2	7/27	1147-1352	0.11	<0.09	7.53	7.64	1.01×10^{-3}
	3	7/27	1455-1659	0.11	<0.10	1.00	1.11	1.46×10^{-4}
	Mean			0.20	<0.10	6.71	7.10	9.26×10^{-4}
	95% Confidence Interval			±0.18	-	±6.37	±6.52	$\pm 8.43 \times 10^{-4}$
Kettle Calciner (1 of 2)								
S13	1	7/27	0920-1020	12.0	1.90	168	182	2.81×10^{-3}
	2	7/27	1219-1324	1.39	4.10	97.0	103	1.43×10^{-3}
	3	7/27	1527-1632	6.46	6.94	105	118	1.72×10^{-3}
	Mean			6.60	4.31	123	134	1.98×10^{-3}
	95% Confidence Interval			±6.01	±2.86	±44	±47	$\pm 8.23 \times 10^{-4}$
Board Dryer Kiln (1 of 1)								
S14	1	7/28	1146-1305	0.47	1.19	12.5	14.1	4.00×10^{-3}
	2	7/28	1425-1622	0.14	0.60	8.41	9.14	2.28×10^{-3}
	3	7/28	1716-1846	0.10	0.61	12.5	13.2	3.47×10^{-3}
	Mean			0.24	0.80	11.1	12.2	3.25×10^{-3}
	95% Confidence Interval			±0.23	±0.38	±2.7	±3.0	$\pm 1.00 \times 10^{-3}$

*$\mu g/Nm^3$ = Micrograms per normal cubic meter (dry gas at 32°F, at as measured O_2 concentration)

#lb/h = Pounds per hour

One can speculate on possible mechanisms, though. As discussed later in this section, the measured mercury losses represented only a small percentage of the total mercury in the raw gypsum feedstock. Perhaps the mercury losses in the dryers and calciner represent a small amount of mercury removed in the wet FGD in the form of elemental mercury adsorbed from the flue gas onto slurry particles, during the intimate gas/slurry contacting in the FGD absorber. Another possibility is that a portion of the oxidized mercury absorbed in the FGD system undergoes reduction reactions after the mercury is deposited on gypsum or solid impurities particle surfaces, to reduce a portion of the oxidized mercury to the elemental form.

The total mercury concentration data show that on a dry gas basis, the concentrations in the kettle calciner steam stack are nominally 100 $\mu g/Nm^3$ or greater, while the two dryer stacks averaged closer to 10 $\mu g/Nm^3$. However, the dry flue gas rate at the kettle calciner stack is much lower than either of the dryer stacks. When the mercury emissions are compared on a mass basis, the losses at the kettle calciner steam stack are only marginally higher than from either of the dryer stacks. Recall that the board dryer kiln stack represents the entire plant production while the dryer mill and kettle calciner steam stacks represent one half of the plant production, so the board dryer kiln mercury emission rate value needs to be divided by two to put it on a similar basis.

Plant Process Data

Plant process data are summarized in Table 7 for the mill tests and Table 8 for the board-line tests. Some of the process data collected during the tests have not been reported here due to their proprietary nature. Note that in the mill, solids feed rates are not measured directly, but are controlled on a relative basis by the speed of the solids feeders, and expressed as a percentage of full feeder speed. However, the mill supervisors can estimate the feed rates based on cumulative weight totals from load cells on the front end loaders that feed the raw gypsum from the gypsum pile, and by the rate of level change in the stucco storage bins compared to wallboard production rates.

Table 7. Task 1 Mill Test Process Conditions

Date	**7/27/2004**	**7/27/2004**	**7/27/2004**	
Time	**0845-1100**	**1145-1400**	**1500-1712**	
Ontario Hydro Run	**Run 1**	**Run 2**	**Run 3**	**Mean**
Dryer Mill A Burner Output, % of full scale	33	33	33	33
Dryer Mill A Feed Rate Output, % of full scale	47	44	42	44
Estimated Dryer Mill Wet Feed Rate, tons/hr	54	51	49	51
Dryer Mill A Dust Collector Inlet Temperature, ^{o}F	177	176	176	176
Dryer Mill A Dust Collector Outlet Temperature, ^{o}F	169	170	171	170
Kettle A Feed Set Point, % of full scale	69	70	70	70
Estimated Kettle Calciner Land Plaster Feed Rate, tons/hr	45	46	46	46
Kettle A #3 (Mid-kettle) Thermocouple, ^{o}F	300	300	300	300

Table 8. Task 1 Board-line Test Process Conditions

Date	**7/28/2004**	**7/28/2004**	**7/28/2004**	
Time	**1146-1305**	**1425-1622**	**1716-1846**	
Ontario Hydro Run	**Run 1**	**Run 2**	**Run 3**	**Mean**
Kiln Speed (board dryer), % of test average	99	100	101	100
Kiln Wet Zone 1 Temperature, ^{o}F	434	437	440	437
Kiln Wet Zone 2 Temperature, ^{o}F	332	333	334	333
Kiln End Temperature, ^{o}F	223	224	224	224

The rates shown in Table 7 for the dryer mill and kettle calciner are based on an estimated 51 ton/hr average dryer mill feed rate for the day-long test, adjusted for the percent moisture to produce a land plaster feed rate to the kettle calciner of 46 tons/hr. The average feed rate for each individual run was adjusted linearly based on percentage feed rate values recorded during that test period, so the average of the three runs would come to 51 tons/hr wet and 46 tons/hr dry. The process conditions shown in Tables 7 and 8 were used as the basis for mercury balance calculations, as discussed in the following subsection. The dryer mill and calciner feed rates, and the board speed in the board dryer represent typical plant operation.

Mercury Balance Results

Table 9 summarizes the mercury balance data for the mill testing. Details are shown on the mercury balance intermediate calculation results, based on input data taken from previous tables in this report. The mercury balance data are shown in several ways. First, the percentage mercury loss from the gypsum solids being processed is calculated, with that percentage being calculated in two ways: one based on the apparent loss by comparing inlet and outlet solids mercury concentrations, and the other based on the inlet concentration versus the Ontario Hydro measurement results for mercury losses from the stacks. The other form of presenting the data is an actual mercury balance, with individual balance closure percentages shown across the dryer mill, kettle calciner, and overall mill. These mercury balances were calculated from the inlet solids mercury concentrations and flow rates, outlet solids mercury concentrations and flow rates, and mercury losses in the flue gases based on the Ontario Hydro results.

The results show that mercury losses across the dryer mill and kettle calciner were low on a percentage basis. The average for the dryer mill was a 1.3% loss of mercury in the raw gypsum calculated from the solids analyses, with a slightly lower percentage of 1.1% being calculated from the Ontario Hydro stack results. For the kettle calciner, the percentage loss was 1.4% based on solids analysis, and 2.3% based on the Ontario Hydro stack results. Therefore, the total mercury loss measured across the mill was only 2.7% based on solids analyses and 3.4% based on Ontario Hydro results from the two stacks.

In general, the mercury balances show excellent closures, particularly considering the measurements were made across a full-scale, commercial plant and that the solids samples were "grab" samples rather than composites over the test durations. The average mercury balance closure was 100% across the dryer mill and 101% across the kettle calciner. Individual measurement run closures were all within ±3% of 100%.

The mercury balance closures across the overall mill were not as tight as the closures across the dryer mill and kettle calciner individually. This may be because there is an intermediate storage silo between the dryer mill and kettle calciner, so there is a time delay between when solids are processed by the dryer mill and when those same solids are processed in the kettle calciner. This effect is most pronounced for the individual runs, since the dryer mill and kettle calciner were sampled simultaneously rather than time phased in an attempt to account for the intermediate storage silo residence time. Individual run mercury balances across the mill overall ranged from 92 to 108% closure, which are still quite acceptable closure percentages. However, on the average for the day, this storage silo residence time had less of an effect on results, as might be expected, with an overall average mercury balance closure across the mill of 102%.

The results of mercury balance calculations across the board line are shown in Table 10. Fewer details about feed rates are shown in Table 10 than in Table 9 due to the proprietary nature of the wallboard forming process. The results show that mercury losses across the board dryer kiln are relatively low compared to the total mercury content of the wet board, with a mean value of 1.9% loss shown in the Ontario Hydro stack results. The solids analyses results show, on average, no loss (-0.9%).

Table 9. Mercury Balance Results for the Task 1 Mill Test

Run Number	Run 1	Run 2	Run 3	Mean	95% C.I.
Feed to Dryer Mill (Raw Gypsum):					
Feed rate, tons/hr	54	51	49	51	±3
Wt% moisture	10.5	10.0	12.6	11.0	±1.6
Hg content, µg/g, dry basis (from Table 2)	0.98	0.94	0.98	0.96	±0.03
Total Hg to dryer mill, g/hr	43	39	38	40	±3
Dryer Mill Product (Land Plaster):					
Dry rate, tons/hr	48	46	43	46	±3
Hg content, µg/g (from Table 2)	0.93	0.93	1.00	0.95	±0.05
Total Hg from dryer mill, g/hr	41	39	39	39	±1
Measured solids Hg loss rate, g/hr	1.73	0.31	-0.71	0.44	±1.38
Measured Hg loss rate at stack, lb/hr (from Table 6)	1.63×10^{-3}	1.01×10^{-3}	1.46×10^{-4}	9.29×10^{-4}	$\pm 8.43 \times 10^{-4}$
Measured Hg loss rate at stack, g/hr	0.74	0.46	0.07	0.42	±0.38
% Hg loss across dryer mill, by solids analysis	4.8%	1.0%	-2.3%	1.3%	±4.0%
% Hg loss across dryer mill, by Ontario Hydro	1.7%	1.2%	0.2%	1.1%	±0.9%
Land Plaster Feed to Kettle Calciner:					
Feed rate, tons/hr	45	46	46	46	±1
Hg content, µg/g (from Table 2)	0.96	0.96	0.98	0.96	±0.014
Total Hg to kettle calciner, g/hr	39	40	41	40	±1
Product Stucco:					
Product rate, tons/hr, calculated	38	39	39	39	±1
Hg content, µg/g (from Table 2)	1.09	1.15	1.14	1.13	±0.03
Total Hg from kettle calciner, g/hr	38	40	40	39	±2
Measured solids Hg loss rate, g/hr	1.11	-0.32	0.62	0.47	±0.82
Measured Hg loss rate at stack, lb/hr (from Table 6)	2.81×10^{-3}	1.43×10^{-3}	1.72×10^{-3}	1.99×10^{-3}	$\pm 0.82 \times 10^{-3}$
Measured Hg loss rate at stack, g/hr	1.28	0.65	0.78	0.90	±0.37
% Hg loss across kettle calciner, by solids analysis	3.4%	-1.0%	1.9%	1.4%	±2.5%
% Hg loss across kettle calciner, by Ontario Hydro	3.3%	1.6%	1.9%	2.3%	±1.0%
Mass Balance Closures:					
Dryer mill Hg closure, output vs. input, %	97%	100%	102%	100%	±3%
Kettle Calciner Hg balance closure, output vs. input, %	100%	103%	100%	101%	±2%
Overall Mill Hg balance closure, %	92%	106%	108%	102%	±10%

Table 10. Mercury Balance Results for the Task 1 Board-Line Test

Run Number	Run 1	Run 2	Run 3	Mean	95% C.I.
Hg in Feed to Board Line:					
Relative Stucco Feed Rate, % of test average	101	99	100	100	±0
Hg Concentration in Stucco, µg/g (dry) (from Table 4)	1.12	1.14	1.10	1.12	±0.02
Hg in Stucco Feed, % of total Hg into Board Line	99.0	99.0	99.0	99.0	±0.0
Hg in Water Added, % of total Hg into Board Line	0.0	0.0	0.0	0.0	±0.0
Hg in Additives, % of total Hg into Board Line	0.5	0.5	0.5	0.5	±0.0
Hg in Paper, % of total Hg into Board Line	0.5	0.5	0.5	0.5	±0.0
Hg in Slurry to Board Forming:					
Hg Concentration in slurry, µg/g (dry) (from Table 4)	1.00	0.98	0.95	0.98	±0.03
Moisture in Set Up Slurry, wt%	30.7	30.9	30.0	30.5	±0.5
Hg in Slurry, % closure with stucco + water + additives	107%	104%	111%	107%	±4%
Hg in Wet Wallboard:					
Hg Concentration in Wet Wallboard, µg/g (dry) (from Table 4)	0.91	0.90	0.91	0.91	±0.01
Moisture in Wet Wallboard, wt%	24.1	26.4	25.5	25.3	±1.3
Hg in Wet Wallboard, % closure with stucco + water + additives + paper	107%	101%	113%	107%	±7%
Hg in Wet Wallboard, % closure with slurry	100%	97%	102%	100%	±3%
Hg in Wallboard Product:					
Hg Concentration in Wallboard Product, µg/g (dry) (from Table 4)	0.94	0.98	0.94	0.95	±0.02
Hg Loss and Balance Closures:					
Measured Hg loss rate at stack, lb/hr (from Table 6)	4.00×10^{-3}	2.28×10^{-3}	3.47×10^{-3}	3.25×10^{-3}	$\pm 1.00 \times 10^{-3}$
% Hg Loss Across Board Dryer Kiln, by solids analysis	0.6%	-7.5%	4.3%	-0.9%	±6.8%
% Hg Loss Across Board Dryer Kiln, by Ontario Hydro	2.3%	1.3%	2.0%	1.9%	±0.6%
Hg Balance Across Board Dryer Kiln, %	102%	109%	98%	103%	±6%
Overall Board-line Hg Balance, output vs. input, %	109%	110%	111%	110%	±1%

The mercury balances across the board dryer kiln showed good closure, with a mean of 103% of the mercury in the dryer feed stream accounted for in the product wallboard and kiln stack flue gas. The mercury balance closure across the overall board line was not as good, with the mercury in the product plus the mercury in the kiln stack gas accounting for a mean value of 110% of the mercury measured in the inputs to the plant.

While 110% is still a very acceptable closure for a trace metal mass balance closure around a full-scale plant, it is apparent that there is a small negative bias in quantifying the total amount of mercury going into the board line in the input streams. For example, the recovery of mercury in the slurry to board forming accounts for 107% of the mercury in the input streams. This represents most of the apparent error in the mercury balance closure across the entire board line.

Summary of Mercury Loss Calculations

The data collected as part of this test were used to calculate an observed, overall percentage mercury loss from the raw gypsum feed during the wallboard production process by two methods. One was to sum the measured losses from the process stacks, as measured by the Ontario Hydro Method, and compare that total to the amount of mercury coming into the wallboard plant in the raw gypsum feed. The data on which this calculation was based are found in Tables 6 and 9. The second method was to compare the mercury concentrations in the raw gypsum feed to the concentrations in the dry wallboard product. Data on which this calculation was based are found in Tables 2 and 4.

Results from these two types of calculations are shown in Table 11. They show a mean loss of 5.1% of the plant input mercury out the three process stacks measured by the Ontario Hydro Method, but only 1.1% loss measured by the change in mercury concentration from the feed to the wallboard product (2.0% after correcting for mercury added with additives and paper in the board line).

Table 11. Summary of Task 1 Overall Mercury Loss During Wallboard Production, Calculated by Two Methods

	Run 1	Run 2	Run 3	Mean	95% C.I.
Total Hg Loss from Process Stacks by Ontario Hydro Method, g/hr*	5.85	3.25	3.27	4.12	±1.69
Total Hg to Wallboard Plant, g/hr#	87	79	77	81	±6
Observed Overall Percentage Hg Loss based on Ontario Hydro Method	6.7%	4.1%	4.3%	5.1%	±1.7%
Hg Concentration in Raw Gypsum Feed to Wallboard Plant, μg/g	0.98	0.94	0.98	0.96	±0.03
Hg Concentration in Wallboard Product, μg/g	0.94	0.98	0.94	0.95	±0.02
Observed Percentage Hg Loss Across Wallboard Plant based on solids analyses	3.5%	-4.2%	3.7%	1.1%	±5.1%
Observed Percentage Hg Loss Across Wallboard Plant based on solids analyses, corrected for Hg added with additives and paper in board line	4.4%	-3.2%	4.7%	2.0%	±5.0%

*Assumes two dryer mill and kettle calciner stacks, one board dryer kiln stack
#Includes mercury in raw gypsum feed plus mercury added by additives and paper in the board line

On first observation, it would seem that the two methods do not agree well with respect to the percentage mercury loss from the wallboard plant feed. However, when the 95% confidence intervals for the mean values from the two calculations are considered, there is considerable overlap in the range for the two methods. The 95% confidence interval for the Ontario Hydro method mean ranges from 3.4% to 6.8% loss, while the 95% confidence interval for the solids analysis method (corrected for mercury added in the board line from the proprietary additives) ranges from –3.0% to +7.0%.

The higher observed variability in the solids data is most likely a result of the calculation approach, which involves quantifying a small number (the mercury loss) by taking the difference between two large numbers (the raw gypsum and wallboard product mercury concentrations). Also contributing to this variability is the fact that the solids samples were small "grab" samples collected from a large process stream, each taken at a particular moment during each Ontario Hydro run. In contrast, the Ontario Hydro measurements represent time-integrated values over periods of one to two hours each.

CONCLUSION

The use of synthetic gypsum in making wallboard has long benefited the environment by recycling the FGD gypsum byproduct, decreasing the need to landfill and increasing the sustainable design of the wallboard product. The increasing numbers of FGD units in the future to further reduce sulfur oxide emissions at the electric utilities will produce greater amounts of synthetic gypsum to either be recycled or landfilled. However, with recent mercury control strategies, this study investigates the potential for mercury to be released into the atmosphere when the synthetic gypsum material is used as a feedstock for wallboard production.

Task 1 evaluated the use of synthetic gypsum from a limestone forced-oxidation FGD system on a plant that fires high-sulfur bituminous coal, with an SCR in service, and does not employ gypsum fines blow down. These results indicated an average of 5% of the incoming mercury was emitted during wallboard production. These losses were distributed across the dryer mill (1%), kettle calciner (2%) and board dryer kiln (2%) as measured by the Ontario Hydro Method at the stack from each process. The measured mercury losses from Wallboard Plant 1 totaled approximately 4 grams per hour, considering that there are two dryer mills, two kettle calciners, and one board dryer kiln.

These mercury losses amount to less than 0.1 lb of mercury emitted per million square feet of wallboard produced or approximately 0.045 grams of mercury per ton of dry gypsum processed. Based on Task 1 results and approximate industry production rates, the wallboard industry would emit less than 1,000 annual pounds of mercury compared to the current power industry emissions of 48 tons reported by the U.S. Environmental Protection Agency. According to this calculation the estimated wallboard industry emissions nears 1% of the power industry emissions. However, Task 1 results represent only one source type and do not embody results for synthetic gypsum from other power plants, coal types and FGD conditions. The estimated industry total emissions will be supplemented as results become available based on the parameters evaluated in subsequent Tasks 2 through 5.

Solids analyses of the raw gypsum feed to the wallboard plant and the wallboard product showed a smaller overall mercury loss of 2% compared to 5% from the Ontario Hydro results. However, the mean percentage loss as measured by solids analyses showed much greater variability than the mean percentage loss calculated from the Ontario Hydro results. When the 95% confidence intervals about the means calculated by the two methods are considered (Ontario Hydro versus solids analyses), the confidence intervals overlap. Thus, the two methods show relatively good agreement when variability is considered.

The mercury mass balance results from Task 1 validate the testing procedures employed, as very good mercury mass balance closures were calculated. This is particularly true for the mill, where the mercury balance closures across the dryer mill and kettle calciner were within ±3% of 100%. The test average mercury mass balance closure across the board line was not as tight as across the dryer mill and kettle calciner but still quite acceptable, within 10% on average across the entire board line and within 3% across the board dryer kiln .

Of the three flue gas streams measured for mercury content by the Ontario Hydro Method, the kettle calciner steam stack showed the highest mercury concentrations, with a mean concentration of 134 µg/Nm^3 when reported on a dry gas basis at actual flue gas oxygen concentrations. Because of differences in mass flow rate and moisture content, the mercury concentration cannot be compared to typical concentrations in coal-fired power plant stack flue gases. The kettle calciner steam stack gas was measured to have a relatively high moisture content of 56%. The mercury concentrations are considerably lower when expressed on a wet flue gas basis, which is the condition under which it is actually released into the atmosphere. Furthermore, the flow rate from this kettle calciner steam stack was relatively low, two orders of magnitude lower than the flue gas flow rate from a typical power plant firing bituminous coal.

Surprisingly, when the mercury emissions are compared on a mass basis, the losses at the kettle calciner steam stack were only marginally higher than from the board dryer kiln stack. The temperature of the board dryer kiln is limited to avoid re-calcining the gypsum to the hemihydrate form and the bulk of wallboard product stays well below 262^oF. Considering that the product temperature is below 262^oF and the board dryer kiln is located downstream of the kettle, significant losses were not expected. It is because of this expectation that the original project design only incorporated board dryer kiln Ontario Hydro stack sampling during Task 1. It is not clear whether or not the proprietary additives, which accounted for 1% of the mercury content of the wet wallboard product, significantly contributed to the small percentage mercury loss measured in the board dryer stack.

It was also surprising that the Ontario Hydro results for all three stacks show the mercury was almost entirely in the elemental form (Hg^0). This is contrary to what was expected given that it is predominantly water-soluble oxidized mercury (Hg^{+2}) that is removed in wet FGD systems, while elemental mercury is virtually insoluble and not removed at significant percentages.

Future testing as part of Tasks 2 through 5 of this project will determine if the mercury loss percentages and mass rates from FGD gypsum used for wallboard production vary significantly for gypsum representing other power plant and FGD conditions. Other conditions include fines blow down from the FGD system, SCR bypassed, low rank coal versus bituminous coal, and lime versus limestone FGD reagent.

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